Electrochemical Investigation and Modeling of LaNi_{4.77}Al_{0.23} Thin-Films Sputtered on Glass Wafers

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Abstract

In the present work, we report on the microfabrication of metal hydride thin-film electrodes which can be utilized for rechargeable microbatteries or sensor applications. A multi-layer deposition technique is developed based on physical vapor deposition to fabricate the thin-film electrodes on a glass substrate. The morphology and the structure of the thin-film electrodes are studied by using Field Emission Scanning Electron Microscopy coupled with an Energy Dispersive Spectroscopy module. The surface composition of the thin-film electrodes are determined using X-ray Photoelectron Spectroscopy. Cyclic Voltammetry and galvanostatic charge-discharge measurements are performed to obtain insights into the electrochemical performance of the electrodes. Finally, a semi-empirical model is derived which allows for the determination of the equilibrium potential of the electrode as a function of its hydrogen content.

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1. Introduction

Micro-Electro-Mechanical-Systems (MEMS) offer many advantages such as size reduction and the capability to integrate a multitude of functions on a single unit while maintaining the potential of being mass produced at relatively low costs. However, one of the technological barriers is the supply of electrical power to microdevices since the power source miniaturization has not kept the same pace. Here, a promising approach seems to be the use of integrated power supplies within the microdevice since only relatively low power and capacity is required; cf. Refs. [1, 2, 3]. Micro-batteries are attractive integrated power sources since their electrochemistry is usually indistinguishable from that of the conventional (macro) batteries and considerable technical knowledge already exists. But configurations, material deposition, post-processing and packaging methods applicable to macro batteries are oftentimes not feasible below the centimeter scale. Thus, the resulting microbattery performance does not proportionally scale at such microscale dimensions [4].

Various microbattery designs exist including two- (2D) and three-dimensional (3D) electrode structures. 3D electrodes increase the capacity of the micro-batteries as reported in Refs [5, 6]. However, the increased complexity in the microfabrication of such 3D microstructures may affect their mass-production adversely. In the 2D (planar) approach, the electrodes are fabricated as thin- or thick-films of electroactive materials that can be deposited by various methods including printing, sol-gel, electrodeposition, physical and chemical

vapor deposition or atomic layer deposition [7].

The present study focuses on the fabrication of a thin-film of a hydrogen-absorbing metal alloy that can be used as an electrode for a rechargeable nickel metal hydride (NiMH) microbattery. Besides the utilization in NiMH microbatteries, this thin-film electrode can be employed for various applications including semi-flow batteries, energy harvesting [8], hydrogen microsensor [9], as well as catalysis [10]. This wide range of applications can be attributed to the excellent reversibility of the hydrogen sorption, in particular, in the case of AB₅-type intermetallic alloys [11]. These AB₅-type alloys, such as lanthanum-nickel compounds (LaNi₅), have a relatively low equilibrium pressure, high storage capacity and rapid reaction kinetics [12]. Hence, they are attractive as battery components. The literature on electrode materials made from LaNi₅ or its derivatives is almost exclusively concerned with metal alloys in bulk or particulate form; cf. e.g. Refs. [13, 14].

The blending of additional elements in LaNi₅ alloys can be beneficial in many aspects, especially when adding small amounts of aluminium Al, cobalt Co or manganese Mn [15, 16]. Liu et al. reported that the partial substitution of Al in the B-site of the LaNi₅ alloy improves not only the cycling performance but also the anti-electro-oxidation and polarizability features [17]. Merzouki et al. added Al and Co and found enhanced life cycles in electrochemical performance measurements [18]. Other research indicated that the Al addition decreases the electrode corrosion due to the formation of a protective oxide layer [19, 20]. Mendelsohn et al. showed that Al addi-

tion overpotential reduces the plateau pressure of the metal alloys [21] which therefore facilitates the activation process [22, 23]. This is of particular interest especially for micro-scale batteries since the in-situ activation of such metal alloy films is not a trivial task [23]. Given the multiple advantages of the Al addition, we choose an $\text{LaNi}_{5-x}\text{Al}_x$ alloy for the current work.

In terms of microsystems, it is desirable to integrate the battery during the device fabrication process using conventional microfabrication techniques and substrates such as silica and glass. Hence, films of $\text{LaNi}_{5-x}\text{Al}_x$ are deposited on glass substrates using the common microfabrication technique Physical Vapor Deposition (PVD) in this work. The deposition of intermetallic alloys films has been reported using various PVD techniques such as Pulsed Laser Deposition [24], Ion Sputtering [25], Ion Plating [26], Radio Frequency (RF) Magnetron sputtering [27], Flash Evaporation-Deposition [28, 29, 30], and Direct Current (DC) Sputtering [31]. The utilization of sputtered intermetallic alloy thin-films is considered as beneficial due to the higher thermal conductivity, the good resistance to hydrogen pulverization, and the formation of protective and catalytic layers as compared to their bulk counterparts [32]. Most of the respective literature rather focuses on the morphologies or the hydrogen sorption characteristics of the deposited films than their electrochemical performance. There are few exceptions such as the study of Sakai et al. [33], who used RF sputtering to produce LaNi_5 and $\text{LaNi}_{2.5}\text{Co}_{2.5}$ thin-films on soda lime, copper or nickel substrates. The crystallinity and capacity of the thin-films depended on the type of target, substrate and sputter parameters. The sputtered films had generally lower

capacities than the respective (particulate) bulk alloy. Furthermore, the film capacity depends on the morphology where an amorphous film was only half of a crystalline film capacity. The authors concluded that this is due to the restricted volume expansion within the film since a peeled-off film could absorb almost the same amount of hydrogen. Wang et al. [32] compared the electrochemical and structural characteristics of $\text{LaNi}_{4.25}\text{Al}_{0.75}$ alloys in powder form and as thin-film deposited by DC magnetron sputtering on a copper substrate. X-ray diffraction (XRD) revealed that both the thin-film and the powder material is crystalline. Simulated battery tests indicate that both exhibit similar electrochemical behavior, possibly due to the fact that both forms have the same crystal structure.

The objective of the present work is twofold: On the one hand, the deposition of films of $\text{LaNi}_{5-x}\text{Al}_x$ alloy on a glass substrate using standard microfabrication methods is investigated. On the other hand, the electrolytic (de-)hydrogenation of these films immersed in aqueous alkaline electrolytes is evaluated. This article continues with a section on the experimental methodologies and materials followed by a thorough material characterization of the fabricated thin-films. Then, the electrochemical performance is characterized by means of Cyclic Voltammetry as well as charge-discharge measurements. Additionally, we derive a kinetic-based model that can be used to infer the equilibrium potential of the MH electrode as a function of the hydrogen content from a single (dis)charge measurement. Finally, the article is summarized with some concluding remarks.

2. Experimental Methods and Materials

In this section, we give a brief overview of the experimental methods and materials which are utilized to fabricate and characterize the thin-films.

2.1. *Thin-Film Deposition*

Microfabrication-grade glass wafers (KB7, UniversityWafer, Boston, MA, USA) with an area of 1×3 square inches are used as substrates for film sputtering. Nickel and chromium targets (Kurt J. Lesker Canada Inc., Concord, ON, Canada) with purities of 99.995% and 99.998% are used to grow thin-films on the glass substrate which serve as current collector and sticky layer, respectively. The intermetallic alloy is custom-made using arch-melting and received in two states from the manufacturer (Kurt J. Lesker Canada Inc., Concord, ON, Canada). That is, as an ingot which serves as the PVD target and as a powder suitable for material testing. The manufacturer reports an elemental alloy composition of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ with a purity of 99.9%. All three targets are 3 inches in diameter while the thickness is 0.125 ± 0.01 inches. The sequential three-layer-film deposition, as sketched in Fig 1a), is performed at NanoFabrication Kingston, ON, Canada, using a magnetron sputtering system (PVD 75, Kurt J. Lesker Co., Pittsburgh, PA, USA). The fabrication process is illustrated in Fig. 1a) and discussed in more detail in section 3.

2.2. *Materials and Physical Characterization*

Investigation of the elemental composition of the deposited metal films is performed with an X-ray diffraction (XRD) instrument (XSPert Pro, Philips

Analytical B.V., Almelo, The Netherlands) via Cu K α radiation. The diffractometer is operated at 40 kV and 45 mA. The raw data is analyzed using the X'Pert Highscore Pro software. An X-ray photoelectron spectrometer (XPS) (Thermo Instruments 310-F Microlab, Newburyport, MA, USA) using the Mg K α method is also applied to gain further insights into the film composition. The surface morphology and elemental composition of the deposited metal alloy films are investigated using a field emission scanning electron microscope (LEO 1530, Carl Zeiss Microscopy GmbH Jena, Germany) equipped with an energy dispersive spectrometer (FSEM/EDS) detector with a resolution of 129 eV at manganese and a light element detection limit of boron. A surface profiler (P-17 Stylus Profiler, KLA Tencor, Milpitas, CA, USA) is employed to measure the thickness of the deposited films.

2.3. Electrochemical Measurements

All electrochemical measurements are performed in aqueous 1 M potassium hydroxide solutions (KOH) (puriss. p.a., 98%, Sigma-Aldrich Canada Company, Oakville, ON, Canada) at a temperature of 23°C using a custom-made three-compartment electrochemical glass cell as sketched in Fig 1b. The working electrode compartment is separated by an ion-conducting media (agar mixed with KOH solution) from the counter electrode compartment to prevent the crossover of the counter electrode reaction products. In preliminary experiments, using a conventional cell, we observed that bubbles barely leave the surface of the vertically-inserted electrode, resulting in a significant reduction in electroactive area. The custom-made cell features a working electrode that is tilted for 45 degrees to the vertical direction so that the bubble detachment is facilitated. Two pieces of nickel mesh are

used as counter electrode (nickel gauze-44128, Alfa Aesar, Haverhill, MA, USA). A mercury/mercury oxide (Hg/HgO) reference electrode (20 wt.% KOH, Northern Material Innovation Ltd., Edmonton, AB, Canada) is immersed in the working electrode compartment via a Luggin capillary. Both working and counter electrode compartments are deoxygenated via bubbling of high purity nitrogen gas (grade 5, Praxair, Danbury, CT, USA) before and during the electrochemical experiments to suppress unwanted side reactions.

Figure 1: a) Fabrication process scheme of the metal hydride electrode and b) experimental setup for electrochemical characterization.

The deposited intermetallic films are electrochemically characterized with Cyclic Voltammetry as well as galvanostatic charge-discharge measurements using a combined potentiostat/galvanostat (VersaSTAT 3 Potentiostat Galvanostat, Princeton Applied Research, Berwyn, PA, USA). In order to eliminate electrolyte as well as contact resistances, IR drop compensation is used based on the current interruption method.

3. Results and Discussion

In this section, we show the results of the material characterization of the target and the deposited films. Then, we discuss our results obtained from the electrochemical characterization and introduce our modelling approach.

3.1. Target Material Characterization

First, the exact elemental composition of the target material is determined in order to compare it with the composition of the deposited films. Fig. 2 shows the XRD pattern of the particulate target material. The multiple distinguishable peaks can be attributed to the presence of $\text{LaNi}_{4.77}\text{Al}_{0.23}$ (hexagonal, $p6/mmm$, 191) in the alloy by matching the XRD profile with the software's reference powder diffraction database for LaNi_5 -type alloys. This elemental composition is reasonably close to the composition of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ that is provided by the manufacturer. From the sharpness of the peaks, it can be inferred that the target material has a crystalline metal structure. Additionally, the XRD results confirms the presence of $\text{La}(\text{OH})_3$ (hexagonal, $p63/m$, 176) and AlNi_3 (cubic, $pm-3m$, 221) in the target. The formation of $\text{La}(\text{OH})_3$ results from exposure of the target to air and takes places in

two steps. In the first step, a partial amount of La undergoes oxidation and forms La_2O_3 . In the next step, the oxide compound converts into $\text{La}(\text{OH})_3$ via a hydroxylation reaction [34]. The formation of AlNi_3 takes place at high pressures and temperatures. Therefore, this compound may have formed during casting of the alloy on the iridium substrate of the target. In order to calculate the phase amounts, the XRD data are fitted using the Rietveld profile fitting method. The calculated phase amounts in the sample material are found to be 61.0% $\text{La}(\text{OH})_3$, 29.2% $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and 9.8% AlNi_3 . The results show that the sample is severely oxidized due to air exposure. However, compared to the actual target (ingot) for the intermetallic sputtering, the XRD sample is in particulate form and has a significantly higher surface area which expedite the oxidation process. Consequently, prior to the actual deposition of the intermetallic alloy on the Ni current collector, we performed a two-minute free deposition to remove the $\text{La}(\text{OH})_3$ layer from the target.

In terms of crystallographic parameters, the lattice parameters and the cell volume are summarized in Tab. 1 and compared with respective results from XRD measurements reported in literature. Generally, there is a good agreement between the results of our measurements and the literature values. The small deviations are within the accuracy of the method and not necessarily a result of the variation in the elemental composition of the alloy.

Figure 2: X-Ray diffraction pattern of the target intermetallic material.

Table 1: Lattice parameters and volume of cell.

Parameter	LaNi _{4.77} Al _{0.23} (This work)	LaNi _{4.7} Al _{0.3} [35]	LaNi _{4.7} Al _{0.3} [36]
a (Å)	5.0260	5.0270	5.02447
c (Å)	3.9980	4.0041	4.00372
Cell volume (Å ³)	87.46	87.6301	87.5

3.2. Thin-Film Deposition

The LaNi_{4.77}Al_{0.23} electrodes consist of multiple layers of different metals fabricated using magnetron sputtering. The process scheme is depicted in Fig. 1a). At first, the glass substrate is subjected to a cleaning process using a solution of DI water, NH₄OH and H₂O₂ at 4:1:1 vol.%. Then, the glass is transferred to the PVD chamber covered with a shadow mask to define the

foot print area of the electrode. We use a rectangular pad that is 2 cm in length and 1 cm in width along with a thin strip that serves as the electrical contact. At first, a chromium layer, which serves as a sticky layer, is grown to a thickness of around 10 nm. Next, a nickel layer with a thickness of 60 nm is sputtered on top of the chromium which serves as the current collector. Finally, the electroactive material $\text{LaNi}_{4.77}\text{Al}_{0.23}$ is deposited. Between each step, the PVD chamber is evacuated to remove traces of previous deposition material which may still be present. The operating conditions used for the different sputtering steps are listed in Table 2. The so-fabricated films have a thickness of 1 μm measured employing the stylus profiler. The mass of the intermetallic film is calculated to be 0.0016 g based on a mass density of 8.24 g/cm^3 . The mass density of the alloy is estimated with two different methods. The first method uses the rule of mixture. This method provides a theoretical upper- and lower-bound of the estimated property, cf. Ref. [37]. The upper- and lower-bound values for the alloy are found to be 8.24 g/cm^3 and 7.66 g/cm^3 , respectively. The second method is based on the crystallography data of $\text{LaNi}_{4.77}\text{Al}_{0.23}$, which are imported in the Match!® software (version 3, Crystal Impact, Bonn, Germany), and the density is calculated to be 8.24 g/cm^3 . Having compared the two methods, the upper-bound value for the density is used in this study. The molar mass of the thin-film is obtained based on multiplication of the molar mass of the atoms by the number of atoms in the alloy; we calculated a molar mass of 425.07 g/mol .

Table 2: Sputtering conditions used for the deposition of the thin-film electrodes..

Parameter	Value		
Material	Cr	Ni	LaNi _{4.77} Al _{0.23}
Vacuum base pressure	$< 10^{-6}$ Pa	$< 10^{-6}$ Pa	$< 10^{-6}$ Pa
Chamber pressure (deposition)	0.4 Pa	0.533 Pa	0.4 Pa
Approx. distance substrate - target	10 cm	10 cm	8 cm
Sputtering method	DC	DC	DC
Sputtering power	150 W	250 W	150 W
Plate Spin rate	20 RPM	20 RPM	20 RPM
Deposition rate	1 Å/s	1.6 Å/s	2.6 Å/s
Substrate temperature (deposition)	20 °C	20 °C	20 °C

3.3. Materials Characterization of the Thin-Film Electrode

The composition and morphology of the deposited intermetallic thin-film electrodes are investigated using EDS and XPS. Fig. 3 shows the emission spectrum along with an inserted FESEM microgram. While most peaks correspond to Ni and La, a small percentage of Al can be seen at around 1.5 keV. Additionally, a small amount of carbon at around 0.35 keV indicates the presence of impurities. Possible impurity sources are the target, slight cross-contamination in the sputter chamber, and impurities in the argon gas used during sputtering. Further EDS measurements at different sections of the electrode confirm that the small amount of carbon is present throughout. Cobalt content is also measured and found to be $0.06 \pm 0.012\text{wt.}\%$ (not visually identifiable in the spectrum).

By offsetting the carbon and cobalt content, the film composition is deter-

Figure 3: Energy Dispersive Spectrum and Field Emission Scanning Electron Microgram (insert) of the sputtered intermetallic thin-film electrode.

mined to be $\text{La}_{1.11}\text{Ni}_{4.73}\text{Al}_{0.19}$. That is, the elemental composition of the deposited films is in good agreement with the sputtering target composition. The insert in Fig. 3 gives an insight into the film's surface morphology. A relatively uniform grain size of roughly 20 nm is observed throughout the electrode surface; i.e., the structure is basically nanocrystalline. Therefore, less mechanical durability is expected compared to amorphous films that resist better to hydrogen pulverization. This is due to the volume increase associated with the hydride formation that leads to mechanical stress in the hydride envelope which surrounds the anhydride core material [28]. Smardz et al. also observed nanocrystalline structures with a comparable grain size

of 15 nm for sputtered LaNi_5 films that are grown at 22 °C and an argon partial pressure of 0.05 Pa [31]. The somewhat larger grain size of our films can be attributed to the higher argon partial pressure of 0.4 Pa that we use for sputtering.

Figure 4: XPS result of the thin-film electrode: a) wide scan of the entire range; b) La(3d) spectrum; c) Ni(2p) spectrum; d) Al(2p) spectrum.

Additional XPS measurements are performed to investigate the elemental composition at the surface of the film electrodes. Here, the carbon offset is taken into account while the satellite peaks are not accounted for. We measure the XP spectra of our samples ex-situ, because the XPS instrument is not coupled with the sputter chamber. The oxidation state of the nickel element at the surface is related to the binding energies and the chemical shifts

in the XP spectra. Schlappbach et al. also observed that the XP spectrum of an air-exposed LaNi_5 powder contains oxidized nickel [38]. Since we do not etch the surface due to the very limited thickness of the films, we also expect the presence of metal oxides at the surface. Fig. 4 gives the XP spectra for the sputtered intermetallic film electrode. In detail, Fig. 4a) shows a wide scan over the entire binding energy (BE) range while part b), c) and d) present the scans over smaller BE ranges that are attributed to La, Ni and Al, respectively. We observe peaks at 841.59 eV and 858.69 eV which correspond to $\text{La}(3d)$ and $\text{Ni}(2p)$, respectively. Furthermore, a much lower binding energy peak is observed at 72.2 eV and attributed to $\text{Al}(2p)$. The BE values that we obtain for $\text{La}(3d)$ and $\text{Ni}(2p)$ are in agreement with those in the work of Smardz et al. [31]. It should be noted that higher binding energy values indicate that the surface of the thin film is slightly oxidized. A $\text{La}(\text{OH})_3\text{-La}_2\text{O}_3\text{-NiO-Al}_2\text{O}_3$ structure is formed which protects the alloy from further degradation [9]. Additionally, we obtain peaks for oxygen and carbon (results not shown). To summarize, the EDS and XPS measurements confirm the presence of La, Ni and Al in the bulk and at the surface of the microfabricated thin-film electrodes. Additionally, these results reveal that a fraction of the alloy surface is oxidized which may affect the electrode performance, for example the activation time. This oxidation may be related to the air exposure after fabrication even though the samples are stored in a (evacuated) desiccator to minimize air exposure.

3.4. *Electrochemical Characterization*

Cyclic Voltammetry of the intermetallic film electrodes are performed in an aqueous solution of 1 M KOH at different scan rates. All currents are

normalized with the mass of the electroactive material of the electrode. It is found that around 10 cycles are required to condition the electrode and to obtain steady and reproducible voltammograms. Depending on the scan rate, very different CVs can be observed. Fig. 5 shows voltammograms at scan rates ranging from 100 $\mu\text{V/s}$ to 100 mV/s and for a potential window of -1.1 to -0.5 V versus Hg/HgO. At low scan rates below 50 mV/s , an oxidation and a reduction peak can be identified. The relatively-broad anodic current peak is observed at a potential of around -0.75 V. The significantly wider cathodic current peak is present at around -0.9 V. When the potential is increased to higher negative values, there is a significant increase of the cathodic current. Generally, the cathodic and anodic current represents the electrolytic hydrogenation (charging) and dehydrogenation (discharging) process at the solid-liquid interface according to the Volmer reaction:

in combination with (de-)hydriding the solid phase. In other words, the anodic peak at around -0.75 V indicates that the adsorbed hydrogen has undergone an electro-oxidative desorption. Here, any consumption of adsorbed hydrogen induces the diffusion of bulk hydrogen to the surface where it can be electro-oxidized as well. The broadness of the anodic peak can be attributed to the relatively slow transport of hydrogen from the bulk to the surface [39]. The cathodic current is related to the electro-reduction of water which results in the adsorption of hydrogen on the electrode surface. Most of these adsorbed molecules diffuse into the metal bulk and form the solid solution until the metal hydride is saturated. With respect to the shape of the reduc-

tion peak in Fig. 5, it is obvious that the electro-reduction of water is not the sole reaction. The hydrogen evolution reaction (HER) has a reduction potential of $E^0 = -0.92$ V versus Hg/HgO and thus occurs simultaneously with the Volmer reaction. Similar voltammograms at relatively-low scan rate can be found e.g. in the work of Kitamura et al. [39] and Thomas et al. [40] for intermetallic (mischmetal) compounds of LaNi_5 and MmNi_5 , produced by arc melting, and a pressed $\text{MmNi}_{4.1}\text{Co}_{0.4}\text{Mn}_{0.4}\text{Al}_{0.3}$ powder-binder mixture, respectively. Obviously there is no influence of the electrode fabrication on the electrolytic (de)hydrogenation process.

It can also be seen in Fig.5 that there are no distinguishable anodic and cathodic (de)hydrogenation peaks for scan rates higher than 50 mV/s. In terms of cathodic reaction, this can probably be attributed to the better performance of the HER. At higher scan rates, the rate of both reactions increases but that of the Volmer reaction is hindered since there is only limited reactant available and supply has to be provided by diffusion through the intermetallic. With respect to the disappearance of the anodic peak, we assume that this is related to electrical double layer charging. The capacitive current is directly proportional to the scan rate and its role at high scan rates can by no means be ignored [41]. Similar behavior is observed in the work of others; though at much higher scan rates. For example, Gamboa et al. [42] and Geng et al. [43] measured the CVs of LaNi_5 in 6 M KOH and found comparable redox potentials and charge densities as in our work. However, the redox current peaks disappeared at a scan rate of 500 mV/s, almost ten times higher compared to our work. This could be related to

Figure 5: Cyclic voltammograms in 1M KOH for intermetallic film electrodes at different scan rates.

considerable differences in terms of electrode fabrication and design. These works used pressed electrodes that were prepared by mixing MH with a compacting (nickel powder) and a carbon binder material. These additives improve the electrode performance, particularly with respect to high-rate discharge [40, 44].

The charge and discharge characteristics of the intermetallic alloy film electrodes are investigated as follows: First, the electrode is subjected to a conditioning step with 10 CV cycles at a scan rate of 1 mV/s. Then,

galvanostatic charge-discharge cycles are performed at a current of 0.5 mA (304 mA/g) which is slightly higher than the exchange current density at fully-charged condition which is discussed in the next section. The respective potential window is chosen to be -1.00 V to -0.57 V versus Hg/HgO.

Figure 6: Electrode potential of the film electrode versus time during charge and discharge with a current density of 304 mA/g.

Fig. 6 gives the first 10 charge-discharge cycles of an experiment with a total of 40 cycles. During the charge step, the potential continuously decreases until it reaches the lower cut-off potential of -1 V where mainly/only

the HER takes place. Then, the film electrode is discharged and the potential continuously increases until it reaches the upper cut-off potential of -0.57 V and the charge process is again initiated. When we inspect a single charge-discharge cycle, the (de)hydrogenation of the film can be clearly assigned to the part of the curve featuring the lowest slope. As it can be seen in Fig. 6, the shape of the cycles slightly changes over the cycle number. This behavior is related to further pulverization [42, 43]. The hydrogen uptake/release in the alloy causes both expansion and shrinkage of the lattice while this mechanical stress may lead to a peristaltic transport of lanthanum to the surface [45]. As a result, the capacity of the electrode also undergoes a slight variation with cycling which is common for metal hydrides [32, 46, 43, 42]. Despite of the lattice change, mechanical degradation of our thin-films is not observed and there is very good adhesion to the Ni current collector even after 40 cycles. The integration of the discharge current density over the time of discharge gives a maximum capacity of 182 mAh/g. For comparison, Wang et al. reported the maximum capacity to be 220 mAh/g in 1 M KOH for a sputtered film of $\text{LaNi}_{4.25}\text{Al}_{0.75}$ on a copper substrate. Sakai et al. reported 160 mAh/g for a RF-sputtered LaNi_5 crystalline film [33]. Capacities of similar powders are typically higher. For example, a maximum value of 290 mAh/g for a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ powder with 5% Ni compacting powder and PVDF binder is reported in Ref. [47]. The lower capacity of sputtered intermetallic alloy films can be explained by the differences in fabrication. As mentioned above, compacting powders, binders and finer grain size can enhance the performance of pressed electrodes. Additionally, the capacity of pressed electrodes is usually reported in 6 M KOH and both electrode sides

are in contact with the electrolyte. Additionally, a percentage of the surface of the thin-film electrode is oxidized (cf. section 3.3) which may cause in a performance loss as well.

When we compare the cycling characteristics of the present thin-film electrode to those of Wang et al. [32, 46], there are some noticeable differences. There is a local potential peak during discharge that we do not observe and their thin-film electrode already shows signs of degradation and capacity variation during the first 10 cycles. The more uniform potential course and better life cycle of our thin-film could be related to the differences in sputtering conditions. In the current study, the deposition is performed with a relatively-low rate of 0.26 nm/s while Wang et al. used a rate of 1.4 nm/s. Higher deposition rate at increased pressure can result in a denser film which has significant volume expansion during pulverization [46]. As a result, the mechanical stability of the so-fabricated film may decrease.

3.4.1. Derivation of an Electrolytic (De-)Hydrogenation Model

In the following, a kinetic-based model for the electrolytic (de)hydrogenation of an intermetallic alloy is derived. The model can be used for material characterization since it allows one to infer the equilibrium potential of the MH electrode as a function of its hydrogen content from a single measurement. The current approach partly follows the work of Yang et al. [48] who modelled the anodic overpotential of MH electrodes for considerable discharge currents; i.e., for large anodic overpotentials. In the current work, we use similar initial assumptions but for small current densities so that (quasi-)steady state conditions of all involved reaction steps can be assumed. Note that a

comparable approach, also based on the work of Yang et al., was reported in Ref. [49], where the authors assumed that the electrode potential during charging equals the equilibrium potential. In contrast, we account for the irreversibilities (overpotentials) which allows to infer the “real” equilibrium potential.

We formulate the model with respect to a discharge measurement of the film electrode but it can be easily re-formulated to work with the charge process. The electrolytic dehydrogenation occurs in three consecutive steps:

1. Diffusion of absorbed hydrogen through the β -phase hydride towards the electrode surface.
2. Transfer of hydrogen from the absorbed sites in the vicinity of the surface to adsorbed sites on the electrode surface according to

3. Electrochemical oxidation of adsorbed hydrogen via the (reverse) Volmer reaction (1).

Since the fabricated thin-film electrodes have very small thicknesses, reaction (1) and (2) are considered as the rate-controlling steps [50]. If the system is in equilibrium, it is characterized by equal rates of H_{ads} production and consumption. By assuming first-order rate reactions, we receive

$$k_2 C_H (1 - \theta) = k_{-2} \theta (C_m - C_H) \quad (3)$$

$$k_1 c_{OH} - \theta \exp\left(\frac{(1 - \beta)F\varphi_0}{RT}\right) = k_{-1} c_{H_2O} (1 - \theta) \exp\left(\frac{-\beta F\varphi_0}{RT}\right) \quad (4)$$

where k_i and k_{-i} denote the rate constants of forward and reverse reaction i , respectively; C_H is the bulk hydrogen concentration (in atoms per metal atom); C_m is the maximum theoretical hydrogen content; θ is the hydrogen coverage at the surface; c_{H_2O} and c_{OH^-} are the concentrations of water and hydroxide in the solution, respectively; F is the Faraday constant; R is the universal gas constant; T is the absolute temperature; β is the symmetry factor and φ_0 is the equilibrium potential.

Inserting Eq. (3) in Eq. (4) to eliminate the surface coverage in favor of the hydrogen content, the following expression can be obtained for the equilibrium potential:

$$\varphi_0 = \frac{RT}{F} \left[\ln \left(\frac{k_{-2}k_{-1}c_{H_2O}}{k_2k_1c_{OH^-}} \right) - \ln \left(\frac{C_H}{C_m - C_H} \right) \right]. \quad (5)$$

On the one hand, even for zero current the equilibrium potential is practically not achieved due to parasitic reactions or sluggish kinetics; these losses can be captured by the equilibrium overpotential η_{eq} . On the other hand, even the smallest (net) current requires that the activation overpotential η_{act} is overcome. Consequently, the electrode potential for sufficiently small current densities can be written as

$$\varphi = \varphi_0 + \eta_{eq} + \eta_{act}. \quad (6)$$

The Tafel equation $\eta(j) = A + B \ln(j/j^\ominus)$ can be used to infer an approximation for the equilibrium overpotential where we normalize the current density j with the exchange current density $j^\ominus$ at the maximum hydrogen concentration in the alloy. At equilibrium state, the current density is zero.

Thus, we cancel the corresponding term and the equilibrium overpotential is approximated to be

$$\eta_{eq} \approx A = \frac{RT}{(1-\beta)F} \ln \left(\frac{j_0}{j^\Theta} \right) \quad (7)$$

where j_0 is the exchange current density. The activation overpotential is modeled using the linearized Butler-Volmer equation according to

$$\eta_{act} \approx \frac{RT}{F} \frac{j}{j_0}. \quad (8)$$

Eqs. (7) and (8) are formulated for the discharge (anodic) process but can be easily reformulated for the charge (cathodic) process. The exchange current density j_0 depends on temperature, electrode characteristics and hydrogen concentration [48]. In this work, we assume that it obeys an Arrhenius-like approach according to

$$j_0 = A_0 \exp \left(\frac{-E_a(C_H)}{RT} \right) \quad (9)$$

where A_0 is a pre-exponential factor and E_a is the activation energy that depends on the hydrogen content of the electrode. Here, the most elementary assumption is that the activation energy correlates linearly with the hydrogen content according to $E_a(C_H) = E_a(C_m) - \kappa \left(1 - \frac{C_H}{C_m} \right)$ where κ is a weight factor. Using the exchange current density at the maximum hydrogen concentration j^Θ , the exchange current density can be re-written as

$$j_0 = j^\Theta \exp \left[\frac{\kappa}{RT} \left(1 - \frac{C_H}{C_m} \right) \right]. \quad (10)$$

which can be used to eliminate j_0 in favor of j^Θ and the hydrogen concentration.

Finally, inserting Eqs.(5,7,8,10) in Eq.(6) and by assuming a symmetry factor similar to 0.5, we obtain the correlation for the electrode potential discharged with sufficiently small current densities as

$$\varphi \approx \frac{RT}{F} \left[A_1 - \ln \left(\frac{C_H}{C_m - C_H} \right) + 2K \left(1 - \frac{C}{C_m} \right) + \frac{j}{j^\ominus} \exp \left(-K \left(1 - \frac{C}{C_m} \right) \right) \right] \quad (11)$$

where $A_1 = \ln \left(\frac{k_{-1}k_{-2}c_{H_2O}}{k_1k_2c_{OH^-}} \right)$ and $K = \frac{\kappa}{RT}$ are regression parameters.

Eq.(11) is fitted to the second cycle of the charge-discharge experiments given in Fig. 6. Here, we use the specific charge content (time) and correlate it to the hydrogen content according to $C_H \left(\frac{H}{M} \right) = \frac{3.6WQ}{F}$ where Q is the specific capacity of the metal hydride alloy in mAh/g and W is the molar mass of the alloy. We also need the exchange current density for the maximum hydrogen content which is measured to be 257 mA/g.

Fig. 7 allows for comparison of the experiments and Eq.(11) using the regression results $A_1 = -30.91$ and $K = -2.07$. We find a very good agreement with the experimental data in most of the concentration range. The model accounts for the non-ideality (slope) of the plateau region and offers a smooth transition between the different regions. Additionally, this model predicts that the activation energy decreases with increasing hydrogen concentration while the exchange current density increases; a consequence of the negative K value. This outcome is consistent with the work of Zhang et al. who experimentally investigated the kinetic parameters of metal hydride electrodes [51]. However, the initial and final stages of the dehydrogenation

Figure 7: Electrode potential versus the hydrogen concentration for a discharge current of 304 mA/g. Comparison of experimental values and electrolytic dehydrogenation model.

are not very well captured; still, the differences are always less than 5%. We assume the deviation to be related to the nonlinearity of the activation energy (exchange current) with the hydrogen concentration in these regions as reported in Refs. [52, 53]. The equilibrium potential versus the Hg/HgO (20 wt.% KOH) reference electrode is obtained by $\varphi_0 = \varphi - \eta_{eq} - \eta_{act}$ and results in combination with the regression parameters in

$$\varphi_0 = -0.800 \text{ V} + \frac{RT}{F} \left[-4.138 \left(1 - \frac{C_H}{C_m} \right) - \ln \left(\frac{C_H}{C_m - C_H} \right) \right]. \quad (12)$$

Here, a similarity with the Nernst equation is obvious. The first term

can be considered as a (standard) potential at defined conditions, while the logarithmic term reflects the concentration correction. The linear function is another concentration correction accounting for the variation of the exchange current density with the hydrogen content of the electrode.

4. Concluding Remarks

This work is concerned with the fabrication and characterization of inter-metallic alloy thin-film electrodes on glass substrates which can be utilized for various microsystem applications. In detail, DC magnetron sputtering is used to deposit a nickel current collector and subsequently a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ film on glass. Energy Dispersive and X-ray Photoelectron Spectroscopy are employed to investigate composition of the film electrodes. The elemental composition is in a good agreement with that of the sputtering target composition but the surface shows traces of oxidation. Furthermore, the films feature a nanocrystalline structure with a relatively-large grain size compared to conventional pressed electrodes. Cyclic voltammograms in 1M KOH show a quasi-reversible hydrogenation and dehydrogenation of the intermetallic alloy thin-film where the performance is similar to comparable conventional electrodes. However, the role of the capacitive current in the thin-film electrodes is more pronounced and the faradaic current is buried at relatively low scan rates. The charge and discharge behavior of the thin-film electrode is evaluated with a current density of 304 mA/g. Even after 40 cycles, we do not find any sign of electrode degradation. The capacity of the thin-film electrode is estimated to be 182 mAh/g which is somewhat lower than that

of comparable regular electrodes. This observation may be attributed to the lower KOH concentration, absence of Ni compacting-powder, the larger grain size of the crystalline structure and the slight oxidation of surface. Performance of the thin-film electrode can possibly be improved by optimizing the sputter chamber pressure and power to grow films with smaller grain size. Finally, a kinetic-based model is derived which allows one to infer the equilibrium potential of the metal hydride electrode depending on the hydrogen content. The model reduces the experimental costs considerably since only one electrolytic (de)hydrogenation measurement at a low current density is required. The model can find applications in material characterization but could also be used for sensors since it correlates electrode potential and hydrogen content of the material.

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6. Nomenclature

A_0	Pre-exponential factor [A/m ²]
A_1	Regression parameter [-]
a	Lattice parameter [Å]
c	Lattice parameter [Å]
C_i	Concentration of component i [mol/m ³]
C_H	Hydrogen concentration [atoms per metal atom]
C_m	Maximum hydrogen concentration [atoms per metal atom]
E^0	Standard potential of reduction [V]
E_a	Activation energy [J/mol]
F	Faraday constant [C/mol]
j	Current density [A/m ²]
j_0	Exchange current density [A/m ²]
j^Θ	Exchange current density at maximum hydrogen concentration [A/m ²]
K	Regression parameter [-]
k_i	Rate constant for reaction i [1/s]
R	Universal gas constant [J/(mol K)]
T	Temperature [K]
W	Molar mass [g/mol]
Q	Specific capacity [mAh/g]

Greek Letters

β	Symmetry factor [-]
η	Overpotential [V]
θ	Hydrogen coverage on the surface [-]
φ	Potential [V]
φ_0	Equilibrium potential [V]

Subscripts

abs	Absorbed
act	Activation
ads	Adsorbed
eq	Equilibrium

Acronym

BE	Binding Energy
EDS	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
HER	Hydrogen Evolution Reaction
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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